Pt(111)-Alloy Surfaces for Non-Activated OOH Dissociation

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We present a density functional theory calculation for the adsorption and dissociation of OOH on Pt(111) and Pt(111)-alloy surfaces. We confirmed the theoretical understanding of an activated OOH dissociation on Pt(111) surface and on small Pt clusters. Interestingly, in this work, we found an existence of a “barrierless” OOH dissociation on several Pt-binary and ternary alloy surfaces with Ru and Mo as alloying components: PtRu and PtRuMo. Here, we demonstrate how such reaction proceeds and discuss the role of Ru–O and Mo–O in the spontaneous OOH dissociation in these systems. The reaction energetics of OOH specie is one of the most sought fundamental surface science studies due to its importance in many catalytic and surface reactions such as hydrogen fuel cell. [DOI: 10.1380/ejsnt.2011.352]

Keywords: Density functional theory; Oxygen adsorption; OOH dissociation; Platinum; Ruthenium-based binary alloy; Molybdenum-based ternary alloys

I. INTRODUCTION

Among the many catalytic and surface reaction processes related to fuel cell development, the adsorption and dissociation of OOH species are considered one of the most important elementary steps. For instance, OOH_{ad} is the main product of the first step in O_2 reduction on metal surfaces [1–3]. It has been observed that the protonation of O_2 comes before O–O bond scission, revealing the utmost importance of OOH dissociation. The energetics of the dissociated components (O_{ad} and OH_{ad}) also significantly influence the over-all reaction as it dictates subsequent reaction steps such as protonation [3, 4] and oxidation of other surface species such as CO [5, 6]. However, most of the fundamental surface science studies are devoted to the understanding of O and OH adsorption on metal or alloy catalysts [7–10], which are generally much simpler to treat. The challenge posed by a more complex OOH adsorption hinders both electrochemical and surface science studies. So far, the OOH adsorption and dissociation is understood on Pt(111) [11] and small Pt clusters [12, 13], where there is a general consensus that the OOH dissociation into O_{ad} and OH_{ad} components is activated. OOH adsorption is also studied in various Pt-transition metal alloys and sandwich structures [14, 16]. In this paper, we first report the non-activated dissociation of OOH on binary and ternary metal alloy systems: PtRu and PtRuMo. By comparison of the reactivity of each of the surface metal alloys and the clean Pt(111) system, we discuss the origin of such reaction.

FIG. 1: (a) Pure Pt surface, (b) PtRu, and (c) PtRuMo. The Pt atoms are numbered and the Mo and Ru locations are depicted in both (b) and (c) accordingly.

II. COMPUTATIONAL METHOD

The theoretical study is based on total energy calculations within the density functional theory (DFT) as implemented in Vienna ab initio simulation package (VASP) [17]. The interaction between ions and electrons is described using projector augmented wave (PAW) method [18, 19]. A plane wave basis set with energy cut-off of 400 eV is used. For the exchange-correlation functional, we employed the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) [20, 21]. As shown in Fig. 1, we considered three model metal surfaces: Pt, PtRu and PtRuMo. PtRu and PtRuMo are denoted as surface metal alloys. The surface atomic ratio mimics the same metal alloy atomic ratio in experiments [22, 23]. Also, theoretically, it conforms to the differences in the segregation energies of Pt, Ru and Mo [24], that is, positive surface segregation energy of the alloying components indicates a considerable number of host metal atom (Pt) on the surface. These fcc(111) metal surfaces are all modeled using supercell approach where

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FIG. 2: OOH_{ad} on (a) pure Pt surface; (b) PtRu; (c) PtRuMo. Top and bottom panels correspond to side and top views of the adsorbate/substrate system. The metal-O1 and O1-O2 bond lengths and the adsorption energies are indicated.

the slab is composed of three atomic layers in a (4×4) unit cell. Because of the periodic boundary conditions imposed via the supercell, a ~ 15.0 Å of vacuum along z -axis is introduced to avoid interaction between surfaces. The surface Brillouin zone integrations were performed on a grid of $(5 \times 5 \times 1)$ Monkhorst-Pack k -points [25] using Methfessel-Paxton smearing [26] of $\sigma = 0.2$ eV. For the adsorption calculations, all the atomic positions are allowed to relax except for the bottom layer, which is constrained to its bulk position. Since adsorption is made on one side of the slab, a dipole correction is introduced. The size of the unit cell leads to an adsorption coverage of $\sim 1/16$ ML with respect to the number of surface atoms. Convergence of numerical results with respect to the slab thickness, the kinetic energy cut-off and the k -point set is established.

III. RESULTS AND DISCUSSION

A. Initial OOH adsorption

The most stable OOH adsorption configuration on the surfaces is exhaustively explored by a potential energy scan on all major sites (top, fcc-hollow, hcp-hollow and bridge) using various OOH conformations with the surface. The potential energy (E_{ads}) is calculated as: $E_{\text{ads}} = E_{\text{system}} - (E_{\text{slab}} + E_{\text{gas-phase adsorbate}})$ where E_{system} , E_{slab} , and $E_{\text{gas-phase adsorbate}}$ correspond to the total energy of the adsorbate/substrate system, bare slab, and isolated molecule, respectively. The adsorption on OOH on Pt(111), in this work, prefers an O-down configuration over Pt top site (see Fig. 2) with the O-O bond tilted up (i.e. end-on adsorption). This structure is in excellent agreement with other DFT results [11]. Because of finite size effects, the adsorption energy slightly differs from that of very small Pt clusters, albeit within the range of those in bigger Pt-cluster sizes [12, 13]. Interestingly,

the end-on adsorption with the O-end of OOH_{ad} (here labeled as O1) is also observed for PtRu and PtRuMo surfaces, but the metal-O1 bond is exclusive to the alloying component. That is, Ru-O1 bond is formed in PtRu while Mo-O1 is formed in PtRuMo. This confirms the “capturing” of O1 by the transition metal atom, X (X: Ni, Co, Cr), which is substituted in a Pt cluster with an atomic ratio (Pt:X) of 2:1 [14]. We note that in PtRu and PtRuMo, the OOH_{ad} is further stabilized, as verified by the shortened metal-O1 bond lengths. Moreover, the O1-O2 (O2 is the oxygen atom attached to H) bond length is already significantly stretched in Pt-surface alloys as shown in Fig. 2, top views. Specifically, the O1-O2 bond length in PtRu is ~ 1.49 Å. This is a ~ 0.03 Å stretch in O1-O2 bond with respect to that of Pt (1.46 Å). For PtRuMo, the O-O bond is elongated by ~ 0.11 Å with respect to PtRu and ~ 0.14 Å with respect to Pt. The role of this elongation at IS in OOH dissociation will be discussed further later.

B. Dissociation of OOH

Next, we calculated the energies of the transition state (TS) and the final state (FS) of OOH_{ad} dissociation into $\text{O}_{\text{ads}} + \text{OH}_{\text{ads}}$ on Pt, PtRu, and PtRuMo surfaces. The transition state is located by determining the saddle point in the minimum energy path towards the final configuration (FS) via potential energy surface (PES) scan. The saddle point is the maximum of the minimum energy path. The exploration of potential minimum involves calculating the potential energy (PE) as a function of the coordinates of the molecule, which represent its degrees of freedom. The variation of coordinates involves changing: (1) the O-OH bond lengths (Δr); (2) OOH distance from the surface (z); and (3) OOH distance from adsorbed state to dissociated state (x, y), with an increment of 0.17 Å. From the calculated PE values, the minimum PE is traced and the point of maximum energy is the TS. Since the location of TS is important for mechanistic study of dissociation, we further checked the TS by displacing the molecule at this point in all possible directions using smaller increments (0.1 Å). Such displacements did not give higher PE. The energies of the three important points in the reaction path, i.e. initial state (IS), transition state (TS) and final state (FS), for Pt(111) is shown in black line in Fig. 3, left panel. Indeed, the dissociation of OOH is activated on Pt. The calculated activation barrier (0.39 eV) for Pt(111) is in good agreement with experiments (0.44 eV [27]) and other DFT results (0.25 eV-0.56 eV [11-13]). However, as shown in the reaction energy diagram for PtRu and PtRuMo, the presence of Ru and Mo on Pt surface remarkably eliminates the barrier. The reaction paths for these metal alloy systems are now downhill from zero PE at certain reaction coordinates. The TS in these flat reaction paths is defined as the starting point for a downhill path. Thus, we show a non-activated dissociation phenomenon for OOH species on Pt metal surfaces in the form of binary and ternary alloys using Ru and Mo as alloying components.

FIG. 3: Reaction diagram for OOH_{ads} into $\text{O}_{\text{ads}} + \text{OH}_{\text{ads}}$ on Pt, PtRu, and PtRuMo. The corresponding transition and final states structures are given on the right. The change in the O–OH bond with respect to IS, is shorter for PtRuMo since O–OH at IS, is already significantly elongated in this system. Since, at PtRuMo, the reaction energy is immediately downhill after the IS, then the defined “TS” is the same as the IS. For, PtRu, the downhill path starts at reaction coordinate ~ 0.40 Å.

C. Dissociation mechanism

Herein, we discuss the details and mechanism of OOH adsorption and dissociation on the model surfaces. First, we note that the trend in the relative stability of OOH_{ad} among the metal surfaces at TS and FS is maintained, that is, with PtRuMo giving the strongest binding, followed by PtRu and then Pt. A careful inspection of the TS and FS of all the surfaces, especially that which involves metal–O2H and metal–O1 bonds, reveals that the metal–OOH interaction is only governed by how much the oxygen (O1) is bound to the surface. At the TS, the metal–O1 bond length decreases in the following order: $\text{Pt} > \text{PtRu} > \text{PtRuMo}$ which suggests that the strength of metal–OOH interaction at TS follows the same order. We note that this metal–O1 bond is the same bond that holds OOH at IS in an end-on configuration, as discussed previously. We recall that, at IS, the O1–O2 bond is already well-loosened. Hence, such IS configurations on Pt-surface alloys seems to contribute to the enhancement of OOH dissociation. The same trend is observed by Balbuena *et al.* [13], wherein the O–O bond elongation in the initial OOH adsorption (IS), although very small (~ 0.01 Å) on pure Pt cluster, correlates well with the decrease the activation barrier for OOH dissociation.

In the following, we show how IS and the TS are correlated. First, we compared the TS and IS for Pt and PtRu. In Table I, we show the charge gained by O1, O2 and H atoms at TS with respect to that of clean Pt using Bader charge analysis [28]. We note that at TS, the O1 atom in PtRu, gains $0.126 e^-$, O2 atom gains $0.052 e^-$ and the H atom gains $0.0 e^-$ with respect to Pt. It is clear that the gain in charge is much more significant in O1 than in O2 and H. To compare PtRu and PtRuMo, we calculated the same gain in charge for each atom as described above. With respect to PtRu at TS, O1 gained more charge ($0.18 e^-$) than that of PtRu with respect to Pt. However, for the case of O2, the gain in charge is

lesser. The presence of Mo (PtRu vs PtRuMo), therefore, increases the net charge in O1 atom but not in O2 and H. The presence of Ru (Pt vs PtRu) increases the net charge in O1 atom and minimally on O2. In all cases, the charge gained by O1 is large whether on PtRu or PtRuMo. Taking all the cases above, we note that IS and TS are correlated via metal–O1 bonding (i.e. Pt–O1, Ru–O1 and Mo–O1). The TS is governed by a large net charge gain on O1, while the IS is governed by significant O–O bond elongation by an end-on OOH adsorption via O1. We note that there is very little difference in the charge density at Mo for PtRu and PtRuMo, hence, the Ru does significantly affect the Mo reactivity to O1.

The next question therefore arises as to how the IS and TS characteristics above affect the energetics of OOH dissociation. First, we note that as OOH adsorbs on the metal surface, the adsorbate orbital splits into bonding and anti-bonding states upon interaction with metal *d*-orbital. It is however in the filling of the anti-bonding states that dictates whether a barrier stands in the way or not, since such occupation results to repulsive O–O interaction. So far there have been no studies on intramolecular charge transfer effects in OOH and therefore, charge transfer between metal and adsorbate is likely. In PtRu, the difference in the charge transferred to the adsorbate at TS with respect to Pt is $0.18 e^-$ (O1+O2+H charges in Table I). For PtRuMo, the charge transfer difference is much larger, $0.34 e^-$. For both cases, the OOH dissociation is barrierless. This suggests that, at least, an increase of $0.18 e^-$ in terms of charge transfer to adsorbate must be achieved to eliminate the barrier in Pt(111).

Since the TS is related to IS via the OOH end-on adsorption by metal–O1 bonding, then, corollary to the charge transfer effects at TS described above, the initial OOH adsorption should lead to an O1–O2 bond length of at least 1.49 Å to lead to an easy dissociation as observed in PtRu. To check whether these limits are reliable, we evaluate the existence of non-spontaneous OOH

TABLE I: Charge gain (e^-) in O1, O2 and H with respect to that of Pt(111) and O–O bond lengths at TS and IS for Pt-surface alloys.

No.	Surfaces	Charge gain (e^-) at TS with respect to Pt			O–O bond at TS (Å)	O–O bond at IS (Å)
		O1	O2	H		
1	Pt	—	—	—	1.80	1.46
2	PtRu	0.126	0.052	0.000	1.79	1.49
3	PtRuMo	0.300	0.037	0.000	1.60	1.60

FIG. 4: Local density of states of isolated OOH and OOH at TS on PtRu and PtRuMo.

adsorption on Pt-alloys previously cited [14]. In all these clusters, the charge transfer to OOH at TS is well below $0.18 e^-$. Specifically, in Pt_2Ni , the charge transfer difference with respect to Pt cluster is $0.09 e^-$, almost the same as that in our Pt(111) calculation. The O–O bond length at initial OOH adsorption in the Pt(111) is $1.457 \text{ \AA}$ (or rounded off to 1.46 in Table I). This is the same as that of Pt_2Ni , which is $\sim 1.453 \text{ \AA}$.

To verify this role of charge transferred to OOH on Pt-surface alloys further, we plotted the local density of states (LDOS) for isolated OOH and for OOH at TS on the Pt-surface alloys as shown in Fig. 4. We note that due to interaction with metal surface, the unoccupied spin down peak (anti-bonding state) right above E_F for isolated OOH, disappears and the unoccupied peak higher in energy is broadened upon interaction with PtRu and PtRuMo. This verifies the occupation of the anti-bonding states via charge transfer from the metal. We also note that the broadening of the adsorbate states are more evident for PtRuMo. This charge transfer mechanism has long been correlated with O–O elongation for many other oxygenated species [13, 29–31]. In particular, for OOH on Pt cluster, the relationship between increasing Pt–Pt distance and elongation of the O–O bond is established [13]. Increasing the Pt–Pt distance shifts the metal d -band closer to the E_F since the Pt–Pt orbital overlap is less when the Pt–Pt lateral distance is increased. If the Pt– d band is close to E_F , the density of states (DOS) at E_F increases, which in turn increases electron states available for charge transfer to the adsorbate.

Lastly, we discussed the importance of the reaction of OOH on metal catalyst. We note that dissociation of OOH with no energy cost is desired in some catalytic reactions. For instance, as mentioned in the introduction,

studies on the presence of OOH in the oxidation reduction reaction (ORR) [32–34] and its selectivity towards water as end product on the cathode of hydrogen fuel cell, present the following elementary steps:

where M represents the metal catalyst. If (2) is slow, then a subsequent protonation would yield $\text{M-H}_2\text{O}_2$ instead of $\text{M-H}_2\text{O}$. This species increases the overpotential on the cathode decreasing the effectiveness of fuel utilization. The presence of H_2O_2 also reduces the effectiveness of the catalyst, reducing the current density of the fuel cell. However, if (1) $\rightarrow$ (2) is spontaneous, then the chance of breaking of OOH into O_{ad} and OH_{ad} before the next protonation, can be enhanced, thus, minimizing the H_2O_2 pathway. Dissociation with least cost of energy is highly required for OOH. In this work, we presented model Pt-surface alloys that can achieve such OOH energetics.

IV. CONCLUSION

We conducted first principles calculation for the adsorption and dissociation of OOH on Pt and Pt-surface alloys: PtRu and PtRuMo. We found that the adsorption of OOH is end-on on all systems. The dissociation of OOH_{ad} into O_{ad} and OH_{ad} is activated on Pt(111) in agreement with experiments and other theoretical works. In this study, we introduce a non-activated dissociation of OOH over PtRu and PtRuMo. The dissociation is spontaneous due to the enhanced Ru–O1 and Mo–O1 bonding (the O by which OOH initially forms bond with the surface). This bonding at IS and TS is governed by an enhanced charge transfer from the alloying component to the OOH via O1. We found that a charge transfer increase (with respect to Pt) of $\sim 0.18 e^-$ in PtRu, eliminates the barrier observed in Pt(111). For PtRuMo, the charge transfer increase is much larger ($0.34 e^-$). The importance of non-activated dissociation of OOH on metal-alloy systems is seen in the oxidation reduction reaction (ORR), which is often desired to be selective towards water formation. The very low cost to dissociate OOH, which is an intermediate in the over-all ORR, prevents H_2O_2 formation and increases the chance for an H_2O pathway.

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